REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 12/16/96	3. REPORT TYPE AND DATES COVERED Journal Article

4. TITLE AND SUBTITLE

Electrosorption of Chromium Ions on Carbon Aerogel Electrodes as a Means of Remediating Ground Water

5. FUNDING NUMBERS

DOE
LLNL Contract No. W-7405-Eng-48

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Lawrence Livermore National Laboratory
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8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

SERDP
901 North Stuart St. Suite 303
Arlington, VA 22203

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

ACS Energy Manuscript No. 960137 Rev.1 (URCL-JC-124565 Rev.2)

11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION / AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE
A

13. ABSTRACT *(Maximum 200 Words)*

An electrically-regenerated separation process has been developed for removing unwanted ions from aqueous waste streams as a minimally-polluting, energy-efficient, and potentially cost-effective alternative to ion exchange, reverse osmosis, electrodialysis, and evaporation. Ground water containing various anions and cations are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area and exceptionally low electrical resistivity. After polarization of the stack, impurity ions are removed from the electrolyte by the imposed electric field and adsorbed on the electrode surfaces. Field tests have shown that hexavalent chromium in the form of $HCrO_4^-$/ CrO_4^{2-}/$Cr_2O_7^{2-}$ can be selectively removed from contaminated ground water with a 530 ppm total dissolved solids (TDS) background. The concentration of Cr(VI) can be lowered from 35 to 2 ppb. The mechanism for Cr(VI) separation involves chemisorption on the carbon aerogel anode, a process that can be reversed by cathodic polarization. Cr(VI) removal is not based upon simple double-layer charging.

14. SUBJECT TERMS

Carbon Aerogel, Electrochemical treatment, Chromium Ions, SERDP

15. NUMBER OF PAGES
29

16. PRICE CODE N/A

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclass.	unclass.	unclass.	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

DTIC QUALITY INSPECTED 1

19980709 108

Electrosorption of Chromium Ions on Carbon Aerogel Electrodes as a Means of Remediating Ground Water

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Abstract

An electrically-regenerated separation process has been developed for removing unwanted ions from aqueous waste streams as a minimally-polluting, energy-efficient, and potentially cost-effective alternative to ion exchange, reverse osmosis, electrodialysis, and evaporation. Ground water containing various anions and cations are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 $m^2 g^{-1}$) and exceptionally low electrical resistivity ($\leq$ 40 mΩ-cm). After polarization of the stack, impurity ions are removed from the electrolyte by the imposed electric field and adsorbed on the electrode surfaces. Field tests have shown that hexavalent chromium in the form of $HCrO_4^-/CrO_4^{2-}/Cr_2O_7^{2-}$ can be selectively removed from contaminated ground water with a 530 ppm total dissolved solids (TDS) background. The concentration of Cr(VI) can be lowered from 35 to 2 ppb, well below the acceptable level for the regulatory surface water discharge limit of 11 ppb. The mechanism for Cr(VI) separation involves chemisorption on the carbon aerogel anode, a process that can be reversed by cathodic polarization. Cr(VI) removal is not based upon simple double-layer charging.

Introduction

Chromium Contamination in Ground Water. Hard ground water (530 ppm TDS) underneath the Lawrence Livermore National Laboratory (LLNL) site is contaminated with trichloroethene (TCE) and 8 to 100 ppb Cr(VI). Air stripping with activated carbon traps is used to remove TCE, while two large ion exchange columns are used to remove approximately 35 ppb Cr(VI). Such pump-and-treat processes are housed in several treatment facilities at LLNL. Water from the wells dealt with during this work were fed to Treatment Facility C (TFC). The ion exchange columns in this particular facility contain 1.7 m^3 (60 ft^3) of mixed resin and have a design capacity of 227 liter min^{-1} (60 gpm). However, the actual feed rate is approximately 57 liter min^{-1} (15 gpm). Regeneration now requires 2,271 liters (600 gallons) of concentrated salt solution with 170,000 ppm TDS every 30 to 45 days. Assuming an average time between regenerations of 37.5 days, the average generation rate of liquid waste with 170,000 ppm TDS is 61 liter day^{-1} (16 gpd), which results in a solid waste generation rate of 10.3 kg day^{-1} (22.7 lb day^{-1}). The solid waste is solid inorganic residue from spent chemical regenerants, the liquid waste, and does not include spent organic ion exchange resins. Significant chromium contamination also exists in the ground water at other sites and must be removed [1]. A variety of electrochemical alternatives to ion exchange are under investigation. For example, polypyrolle films on reticulated vitreous carbon electrodes are being used for in situ reduction of Cr(VI) [2].

Unfortunately, this approach suffers from gradual degradation of the electrodes due to a loss of polypyrole. Another process involves the use of electrodes coated with films of electroactive ferrocyanide for selective removal Cs^+ from solutions of sodium salts [3]. Here too electrode life is limited by the stability of the electroactive film. Carbon aerogel electrodes appear to have the necessary selectivity and stability to enable them to serve as a viable alternative to ion exchange. During investigtions with activated carbons, others have observed high electrosorption capacities for alkali metal cations than for the associated anions, and attributed the differences to the presence of carbonyl groups on the surface. It is believed that the selectivity for chromium observed during this investigation is due to complexation of the oxygen-containing chromium ions with various functional groups on the carbon surface. In additional to carbonyl groups, the carbon surface may also have hydroxyl groups. The exact nature of the comlexaton is not well understood, though it is assumed to involve formation of a weak bond between the Cr, O or H atoms in the ion with C, O or H atoms in the surface.

Early Development with Activated Carbon Electrodes. Several publications and patents have appeared that discuss the use of porous electrodes for the recovery of heavy metals from aqueous solutions by electrodeposition [4-11]. The first studies on retention of ions in the electric double layer appear to have been published at the University of Oklahoma in the early 1960's [12,13]. The application of interest was desalination of brackish water. The detailed report by Caudle et al. describes flow-through capacitors with porous, activated-carbon electrodes [13]. Inert polymeric binders were used to hold the carbon particles together in thin conductive sheets. Johnson et al. conducted similar studies with beds of activated carbon and published their work in early 1970's [14-16]. Their experimental program included verification of the theoretical basis for the process, parametric studies, and evaluation of a variety of candidate electrode materials. Johnson's work prompted Newman to develop a comprehensive theoretical model for the capacitive charging of porous carbon electrodes [17]. Though this process was eventually abandoned by Johnson due to various problems, including the failure to demonstrate degradation-free electrode performance, preliminary cost studies did indicate that an efficient, low-cost desalination plant based upon this technology could be built if adequate durability of the electrodes could be achieved. Work on desalination with porous, activated-carbon electrodes was done in Israel several years later and published in the 1980's [18-20]. A column was built from two separated vertical beds of activated carbon, one serving as the anode and the other serving as the cathode. Concentration ratios as high as 1/100 were attained between the top and the bottom of the column. Since this work was conducted decades before the invention of carbon aerogel electrodes, such materials were not included in the study. More recently, carbon aerogel electrodes developed by LLNL have also been employed in a variety of configurations to remove ionic contaminants from water [21-27].

Problems Encountered with Activated Carbon Electrodes. Several practical problems are encountered with conventional activated carbon electrodes. For example, polymeric binders occlude significant fractions of the activated carbon surface [12,13]. Such electrodes have characteristically high electrical and mass transfer resistances. Furthermore, polymer binders are susceptible to both chemical attack and radiation-induced degradation, a problem that would be encountered during the removal of dissolved radionuclides. Fluorinated polymers are more susceptible to radiation damage than polyethylene and polystyrene. Systems that use flow-

through beds of activated carbon powder as electrodes require membrane separators for electrical insulation and to prevent entrainment of individual particles in the flow [14-16]. Even so, smaller particles generated by erosion of the primary particles can become entrained, thereby depleting the bed. Since raw water is flowed in the axial direction through the beds, a large pressure drop develops. Unfortunately, activated carbons appropriate for use in beds with low pressure drop also have relatively low specific surface areas. Furthermore, process efficiency is lowered by the large potential drop that develops in thick electrodes and packed beds. Even though adjacent carbon particles may touch, intimate electrical contact may not exist. Consequently, the electrical resistance can be high. Channeling is also encountered with such systems.

Advantages of Carbon Aerogel Electrodes. The unique optical, thermal, acoustic, mechanical, and electrical properties of aerogels are directly related to their unusual nanostructure, which is composed of interconnected particles with microscopic interstitial pores [28-32]. Carbon aerogel is an ideal electrode material because of its low electrical resistivity (≤ 40 mΩ-cm), high specific surface area (400 to 1100 m^2 g^{-1}), and controllable pore size distribution (≤ 50 nm). Note that surface areas greater than 2600 m^2 g^{-1} are now possible with special chemical and thermal activation [33]. The exceptionally high conductivity of carbon aerogel, in contrast to loosely bonded carbon powders or activated carbon fiber cloths (ACFCs), is attributable to its monolithic structure which is composed of interconnected, covalently-bonded carbon particles (~12 nm diameter). Electrical conduction takes place by the drift of delocalized charge carriers within carbon nano-filaments, as well as by the transfer of carriers from one large conducting segment to another by hopping or tunneling. In contrast to electrodes made from activated carbon powders and fibers, the activation energy for carrier transport in carbon aerogel is relatively small. As a result of these desirable characteristics, carbon aerogels have already been used as electrodes in supercapacitors with high energy and power densities [34]. Numerous supercapacitors based on various porous carbon electrodes, including carbon aerogel electrodes, have been developed for energy storage applications [35-39]. However, none of these devices was designed to permit electrolyte flow and most required membranes to physically separate the electrodes.

Electrosorption on Carbon Aerogel Electrodes. Electrochemical cells with carbon aerogel electrodes have been used previously by LLNL to remove a variety of contaminants, including NH_4ClO_4, from aqueous waste streams [21-27]. The solution to be separated was passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m^2 g^{-1}) and very low electrical resistivity (≤ 40 mΩ-cm). In some cases involving non-reducible and non-oxidizable ions, anions and cations were removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes. However, in other cases involving large polyvalent oxyanions, heavy metals and colloids, impurities were removed by a combination of double-layer charging, physisorption, chemisorption, electrodeposition and electrophoresis. During feasibility tests with contaminated ground water in the laboratory, it was demonstrated that the concentration of hexavalent chromium ($HCrO_4^-$ /CrO_4^{2-}/$Cr_2O_7^{2-}$) could be lowered from 35 to 2 ppb, well below the acceptable level of 11 ppb. Subsequently, a successful field demonstration was conducted at LLNL Treatment Facility C.

Three stacks of 48 double-sided carbon aerogel electrodes were polarized at +1.2 V and used to continuously remove Cr(VI) and Cr(III) from raw, untreated ground water. Note that the anodes and cathodes are identical and that the +1.2 V applied to the cell is relative. A positive voltage implies polarization in one direction, while a negative value implies polarizaiton in the opposite direction. Application of the voltage difference between adjacent pairs of electrodes induces an electric field normal to the electrodes, which forces cations to move towards the cathode and forces anions to move towards the anode. The exact speciation of the chromium ions depends upon pH, temperature, concentration, and the presence of other ions. However, it is believed that Cr(VI) is in the form of $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$, while Cr(III) is in the form of $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_4^-$ or CrO_2^- [40-42]. This is discussed in more detail in a subsequent section, in regard to Figure 2. Transport of anions and cations to the surfaces of their respective electrodes is by convetion, diffusion, and electromigration, with the relative rates primarily dependent upon the size and charge of ions. Once at the surface, the ions can undergo complexation, and electrochemical reaction in some cases. Since all Cr(VI) species are anionic, they would be drawn to the anode. Since these anions are already in a high oxidation state, complexation at the anode without any anodic oxidation would be expected. In contrast, Cr(III) species are both cationic and anionic. Since cationic species are already in a low oxidation state, complexation at the cathode without any cathodic reduction is expected, though reduction to metallic adatoms of Cr is possible in some circumstances. However, trivalent anionic species such as $Cr(OH)_4^-$ and CrO_2^-, would be forced to the anode where anodic oxidation to $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$ would be possible. The hexavalent species would then be complexed. In addition to these postulated mechanisms, the cathodic reduction of Cr(VI) anions has been observed. Transport of these species to the cathode wold be dominated by convective and diffusive transport. After saturation of the stack, regeneration was accomplished by the following sequence: (a) cell discharge at 0 V; (b) reverse polarization at -1.2 V; and (c) cell discharge at 0V. Since discharge at 0 V was insufficient to release the complexed chromium, it is evident that the operative separation mechanism is not due to simple double-layer charging. The need for reverse polarization, which could cause cathodic reduction on one electrode and anodic oxidation on the other, implies that the release involves charge transfer reactions, and a probable change in functionality at the carbon surface. These mechanisms are discussed in greater detail in subsequent sections. It has also been shown that copper, zinc, nickel, cadmium, chromium, lead and uranium can be removed from sea water and 0.1 M KNO_3 [27]. This electrolytic separation process has several potential advantages over other more conventional technologies. Since regeneration is accomplished by electrical discharge or reverse polarization, no secondary waste is generated. This is in sharp contrast to ion exchange, which requires concentrated solutions of salt, acid, or base for regeneration of the resin. Furthermore, this approach is believed to be much more energy efficient than evaporation and offers operational advantages over reverse osmosis (RO) since high-pressure pumps and membranes are not necessarily required [25,26]. The undivided cells used in this investigation required no membranes.

Limitations of BET Surface Areas. It is noteworthy that activated carbon powders with Brunauer-Emmet-Teller (BET) surface areas as high as 3000 m^2 g^{-1} are readily available. However, much of the surface area in such materials is located inside pores having diameters less than 1 nm. It is believed that the electrochemically active area is only a fraction of the BET surface area. BET analyses are probably misleading since gas molecules can penetrate much

smaller pores than a typical electrolyte. For example, the bond length of N_2 is only 0.1 nm. It is very doubtful that this level of porosity contributes to electrochemical double layer formation since electrolyte penetration and double layer formation are questionable on this scale [25,26]. From the Gouy-Chapman theory, as well as the Stern modification of that theory, it is believed that a fully-developed electric double layer on a planar electrode with no detrimental shielding effects would require much greater distances for full development [43]. In the case of a 1:1 electrolyte in water at 25°C, the characteristic thickness of the diffuse layer ranges from 1 nm at a concenetration of 10^{-1} M to 30 nm at 10^{-4} M. Finally, published capacitance-density data indicates that the double layer at the carbon-electrolyte interface is primarily formed in the mesopore region [28]. In the specific case of dissolved Cr(III) and Cr(VI) species, the ions alone probably have cross sections with 0.4 to 0.6 nm diameters. These estimates are bsed upon representative Cr-O and Cr-Cr bond lengths, which are 0.157 and 0.250 nm, respectively [44]. Since these ions will be accompanied by water molecules, the minimum pore size required for penetration, ignoring electrostatic shielding, will probably approach a minimum of 1 nm, 10X greater in size than the N_2 molecules used for BET surface area determinations.

Experimental

Synthesis of Carbon Aerogel. Thin sheets of carbon aerogel composite (CAC), a novel material developed by LLNL, were synthesized by infiltrating a 70% w/v resorcinol-formaldehyde (RF) solution into a porous carbon paper (Textron Specialty Materials, Lowell, MA, for example). After infiltration, the RF/carbon paper was cured between glass plates in a closed vessel which prevented evaporation. The cured paper was then exchanged into acetone, which was subsequently evaporated at room temperature. Finally, the RF/carbon paper was pyrolyzed at 1050°C in a nitrogen atmosphere. This fabrication process resulted in monolithic, open-cell structures composed of chains of interconnected carbon particles with characteristic diameters of ~10 nm. This unique material has a high specific surface area (400-1100 $m^2 g^{-1}$), an optimal pore size (~50 nm), and an exceptionally low electrical resistivity (40 mΩ-cm). In fact, the resistivity is so low that it may be possible to eventually eliminate the titanium plates used as supports in this study. Each sheet of CAC was 6.86 cm x 6.86 cm x 0.0127 cm, had a total active surface of approximately 2.8×10^6 cm^2, and had a through (front-to-back) resistance of about 10 μΩ.

Fabrication of Electrodes. Double-sided electrodes were made by gluing two sheets of CAC to both sides of a titanium plate that served as both a current collector and a structural support. A thin film of conductive, graphite-filled epoxy was used as the adhesive. After gluing, the epoxy was cured for 24 h at 85°C. It is important to note that the titanium surface does not participate in the chromium removal since it is covered by graphite-filled epoxy and carbon aerogel (CAC sheet). Any exposed titanium area is relatively insignificant.

Construction of Electrochemical Cells. Figure 1 is a schematic representation of a stack of double-sided electrodes similar to the ones used in this investigation. A published photograph can be found as Figure 2 in Reference 26. Note that these cells are undivided and use no membranes. A pattern of holes was located around the perimeter of each titanium plate and accommodated 12 threaded rods that held the stack together. Even electrodes served as cathodes

while odd electrodes served as anodes. The electrodes and headers were aligned by the threaded rods. A separation of about 0.12 to 0.16 cm was maintained between electrodes by rubber compression seals (gaskets) and cylindrical Delrin (acetyl resin) spacers concentric with the threaded rods. Note that the height of each spacer, measured from shoulder to end, was 0.127 cm (0.050 inches). A rectangular orifice in each titanium plate admitted flow into the downstream electrode gap. This orifice was located inside the pattern of holes, as well as inside the rubber compression seal, and was aligned with one edge of each CAC sheet. Since the orifices alternated from one side of the stack to the other, the flow path through the stack was serpentine. Note that the orifice was divided by a center tab. The field test used three assembled stacks that had a total of 144 double-sided electrodes (288 sheets of CAC; 144 individual electrochemical cells). The total quantity of carbon aerogel used in the experiment was about 144 grams of carbon (1.36 m^2 or 14.6 ft^2 of CAC sheet). The liquid inventory contained by the cell was approximately 1 liter (1,063 ml). Flow through the stack was driven by line pressure generated by a pump at the well head. The flow rate was approximately 100 ml min^{-1} during chromium removal and 100 to 1000 ml min^{-1} during regeneration. All lines were made of Teflon and had a nominal diameter of ~10 mm (1/4 inch). The cells were polarized by a programmable power supply that had a voltage range of 0 to 12 V or a current range of 0 to 60 A. Most specialty components were made at LLNL. The power supply, pumps, conductivity and pH sensors were obtained commercially. Any high-quality generic power supply, pump, and sensors should suffice.

Analytical Measurements. Temperature, electrical conductivity and pH were continuously monitored by means of sensors placed on the inlet (feed) and outlet (product) lines of the stack. During the experiment, samples of both the influent and effluent waters were withdrawn and analyzed for various constituents at LLNL and California Laboratory Services in Rancho Cordova, California. The constituents of primary interest [eg., total Cr and Cr(VI)] were measured at the LLNL Environmental Chemistry Laboraory, and the methods used are summarized in Table 1 [45-47].

Table 1. Primary methods used to analyze the TFC waters during this investigation.

Analyte	EPA Method No.	Technique	Detection Limit (ppb)	Ref.
Cr(VI)	7196	Colorimetric	2	45
Total Cr	218.2	AAS Furnace	1	46
Zn	289.2	AAS Furnace	1	46
Halocarbons	601	Purge & Trap, GC	0.1 to 4	47
Aromatics	602	Purge & Trap, GC	0.1 to 3	47

Atomic absorption spectroscopy was used to measure the total concentration of chromium as specified by Environmental Protection Agency (EPA) 218.2. The detection limit was approximately 1 ppb. Aqueous spectrophotometry was used to measure the concentration of Cr(VI) alone as specified by EPA 7196. The detection limit of this standard method for Cr(VI) was lowered from 5 to 2 ppb by the use of a spectrophotometer cell with a 5 cm optical path. A full suite of quality control samples was analyzed during the application of these methods.

Samples used for the measurement of heavy metals were collected in 500 ml plastic containers. Metals regulated by the National Pollutant Discharge Elimination System (NPDES) were determined by 200 Series EPA Methods. These samples were collected in 1 liter plastic bottles and acidified. Samples for this analysis of organics were collected in 40 ml glass vials and measured by EPA Methods 601 and 602. All samples were kept on ice until analyses could be performed.

A typical analysis of the influent water is given in Tables 2a and 2b. Attempts were also made to measure Ag, Al, As, Be, Cd, Co, Cu, Fe, Hg, Mo, Mn, Ni, Pb, Se, Sb, Tl and V; however, none were detected. It is assumed that they were below the analytical detection limit, if they were present at all.

Table 2a. Overall characteristics of the water treated during this investigation.

pH	7.5
Specific Conductance	840 μS cm^{-1}
Total Dissolved Solids (TDS)	560 mg liter^{-1}
Hardness (as $CaCO_3$)	220 mg liter^{-1}
Total Alkalinity (as $CaCO_3$)	270 mg liter^{-1}
Bicarbonate (as $CaCO_3$)	270 mg liter^{-1}

Table 2b. Concentrations of specific analytes in the water treated during this investigation.

Analyte	Concentration (mg liter^{-1})
Na	110
Ca	56
Mg	19
K	1.7
Zn	0.03
Cl	140
SO_4	41
NO_3	24
P as PO_4	1.1
F	0.55
NO_2	<0.5

The detection limits for various heavy metals were approximately 1 ppb (1 μg liter^{-1}), whereas the detection limit for organics was quoted as 0.2 ppb (0.2 μg liter^{-1}). It appears that chromium concentrations could usually be determined within $\pm$ 2% (98 to 102% recovery), based upon periodic measurements of standards with known concentrations. Similar recovery data for the organics indicates that the concentrations of those species could be determined within 4 to 6%. Measurements of standards were made throughout the test to assure reliability of the analytical results. The specific conductance of the feed and product was determined on line with a flow

through conductivity cell with a 1 cm^{-1} cell constant and a standard electronic meter with an analog output. In most cases, conductivity, pH, temperature, voltage and flow were determined within: $\pm$ 1 μS cm^{-1}; $\pm$ 0.01 pH unit; $\pm$ 0.1 °C; $\pm$ 0.01 V; and $\pm$ 1 ml min^{-1}, respectively. During the experiments, a gas collection apparatus was installed in the outlet line of the electrosorption equipment, but no significant gas evolution was observed at any of the applied voltages.

Results

Figure 2 shows a plot of the concentrations of both Cr(VI) and Cr(III) in the outlet stream during the first 28 h of operation. As previously discussed, Cr(VI) is in the form of HCrO$_4^-$/CrO$_4^{2-}$/Cr$_2$O$_7^{2-}$, whereas the Cr(III) is in the form of Cr(OH)$^{2+}$/Cr(OH)$_2^+$/Cr(OH)$_4^-$/CrO$_2^-$ [40-42]. The possibility of forming non-ionic chromium hydroxide monomer, dimer, trimer, and tetramer is also recognized. Essentially all of the chromium in the inlet stream was Cr(VI), because the total Cr measured by atomic abosorption spectroscopy (AAS) was nearly the same as the Cr(VI) measured by colorimetry. There was no significant change in the chromium during the initial open-circuit period. Immediately following polarization at 0.9 V, the total concentration of chromium in the outlet stream dropped from 30-35 ppb to less than 10 ppb. The concentration then started to trend upward. The speciation of chromium in the outlet stream was approximately 30% Cr(III) and 70% Cr(VI). After operating the cells at 0.9 V for 8 h, the polarization was increased to 1.2 V. The additional polarization lowered the total concentration of chromium in the outlet stream from 15 to 8 ppb, while the concentration of Cr(VI) in the outlet dropped from 12 to 5 ppb. The concentration of Cr(VI) remained below 7 ppb during the 28 h shown in the figure, whereas the total concentration of chromium remained below 10 ppb. It is evident that in addition to removing Cr(VI) from the stream of water, Cr(VI) was reduced to Cr(III). Furthermore, the chromium removal continued long after saturation of the carbon aerogel with other ionic species, indicating a high degree of selectivity towards chromium. Data at such low concentrations must be interpreted carefully. In regard to the Cr(III) and Cr(VI) measurements, most were made within $\pm$ 1 ppb. In periodic measurements of feed samples, taken upstream of the electrochemical cell, essentially all of the chromium was in the form of Cr(VI). The total chromium and Cr(VI) were essentially the same in these samples. However, samples taken downstream of the electrochemical cell showed significant differences. Thus, the observed differences are believed to be real.

Figure 3 shows a plot of the concentrations of both Cr(III) and Cr(VI) in the outlet stream during an extended period of 250 h. The concentration of Cr(VI) remained below an acceptable level of 11 ppb (surface discharge limit) for more than 50 h of operation, whereas the total concentration of chromium remained below 17 ppb. The concentration of Cr(VI) was not acceptable after 50 h of operation since it was greater than the surface discharge limit. After 200 h of operation, the concentration of Cr(VI) gradually increased to a level slightly below 20 ppb, while the total concentration had increased to almost 30 ppb. It is believed that the increase in chromium concentration in the product stream with time was due to the gradual approach to equilibrium at the interface between the electrolyte and the carbon aerogel. Since the overall electrosorption capacity after regeneration was comparable to that prior to the test, there was no apparant loss of carbon mass and active area, which could have been another plausible explanation for the

observed trend in chromium concentration. Similar results were obtained in a preliminary laboratory experiment. In other published studies, such CAC electrodes have been operated semi-continuously for several months without substantial *permanent* losses in capacity [25].

Figures 4 and 5 are shown to illustrate the fact that the electric double layers are completely formed early in the experiment, prior to establishing equilibrium between dissolved and adsorbed Cr(VI) and Cr(III) species. Transients in the conductivities of the inlet and outlet streams, as well as the cell voltage as a function of time, are shown in Figure 4. The stacks were operated without polarization (open circuit) for the first 4 h, then at +0.9 V for 8 h, and finally at +1.2 V for the remainder of the treatment time. The conductivity of the inlet steam remained between 850 and 900 $\mu S \ cm^{-1}$ during the entire experiment. Before polarization, the conductivity of the outlet stream was lowered to about 780 $\mu S \ cm^{-1}$ by the chemisorption of ions on the unpolarized carbon aerogel electrodes. After the surface of the carbon aerogel became saturated with adsorbate, the conductivity started to increase. During the first 4 h without polarization (open circuit), the conductivity gradually increased to approximately 925 $\mu S \ cm^{-1}$, a level slightly greater than that of the inlet stream. The "overshoot" was due to concentration of the ions during desorption from the carbon aerogel. After the cells were polarized at 0.9 V, the conductivity of the outlet stream dropped to a level between 650 and 700 $\mu S \ cm^{-1}$, and then increased as the double layer charged. The polarization was increased to +1.2 V and the conductivity passed through another minimum, about 800 $\mu S \ cm^{-1}$. It should be noted that chromium ions at a concentration of 35 ppb will have very little effect on the conductivity of a solution with 530 ppm dissolved salt. The contributions of chromium ions to conduction in the solution is orders-of-magnitude less than the contribution of other impurities. Typically, the conductivity of an electrolyte increases about 1 $\mu S \ cm^{-1}$ for every ppm increase in salt concentration.

Transients in the pH of the inlet and outlet streams, as well as the cell voltage as a function of time, are shown in Figure 5. The pH of the inlet steam remained between 7.4 and 7.5 during the entire experiment. Before polarization, the pH of the outlet stream was lowered to 6.6 by the chemisorption of ions on the unpolarized carbon aerogel electrodes. After the surface of the carbon aerogel became saturated with adsorbate, the pH gradually increased to 7.4, essentially the same as that of the inlet stream. The initial suppression of pH was due to the chemisorption of alkaline ions from the ground water. After the cells were polarized at 0.9 V, the pH of the outlet stream dropped to a level between 6.9 and 7.0. The pH again gradually increased to that of the inlet stream. The pH of the outlet stream dropped to a level between 6.8 and 6.9 after the polarization was increased to 1.2 V after 10 h. The pH of the outlet stream always decreased after polarization, indicating saturation of the carbon aerogel surface by anions that contribute to the alkalinity of the solution. Trends in the pH of samples taken to the analytical larobratory for measurement followed trends in the on-line pH measurements, but were higher by approximately 0.6. As expected from earlier work, trends in pH and conductivity were well correlated.

As shown in Figure 6, the carbon aerogel electrodes were regenerated by a three-step voltage sequence after more than 382 h of operation. Regeneration was done at 382 hours to assure equilibrium of the CAC surface with the flowing well water so that a credible determination of the electrosorption capacity could be made. The total concentration of chromium in the inlet

stream, which was essentially all Cr(VI), remained between 30 and 35 ppb during the entire 396 h of operation. After more than 384 h of operation, the cells were discharged by connecting the anodes and cathodes through a power resistor (0 V and 100 ml min⁻¹). Though the concentration of Cr(VI) in the outlet stream did not increase, the total concentration of chromium increased to almost 200 ppb. Surprisingly, most of the chromium released during the first regeneration at 0 V was in the form of Cr(III). After 390 h of operation, the cells were reverse polarized (-1.2 V and 1000 ml min⁻¹). This caused a sudden increase in the concentration of Cr(VI) in the outlet stream, as well as a corresponding increase in the total concentration of chromium. After the reverse polarization, a second regeneration at 0 V released the remaining chromium, which was primarily in the form of Cr(VI). Cr(III) was held electrostatically in the electric double layer, whereas Cr(VI) was held by chemical complexation. Discharge of the cell at 0 V (removal of the imposed electric field) released the Cr(III), but not the complexed Cr(VI). Reverse polarization caused cathodic reduction at the electrode complexed with the Cr(VI) species, thereby destroying the CAC-Cr(VI) bonds. The accumulation of chromium in the stack of carbon aerogel electrodes, Figure 7, was calculated by numerically integrating the concentration-time data, Figure 6. The formula used is given as Equation 1:

$$\Delta m(t) = \int_0^t F(t)\{C_{in}(t) - C_{out}(t)\}dt \qquad [1]$$

where $\Delta m(t)$ is the accumulation of chromium, $F(t)$ is the flow rate through the stack of electrodes as a function of time, $C_{in}(t)$ is the concentration of chromium in the inlet stream as a function of time, and $C_{out}(t)$ is the concentration of chromium in the outlet stream as a function of time. This integral mass balance shows that most of the chromium was recovered after regeneration by (1) discharge at 0 V and 100 ml min⁻¹, (2) reverse polarization at -1.2 V and 1000 ml min⁻¹, and (3) discharge at 0 V and 1000 ml min⁻¹. It must be noted that the flow rate of 1000 ml min⁻¹ during the third regeneration step had to be assumed based upon written instructions and the recollection of the operators since no flow rate was recorded on log sheets. The flow rate was not changed after the reverse polarization at -1.2 V and 1000 ml min⁻¹. The results in Figure 7 show outstanding accountability for the Cr impurity removed from the well water.

Figure 8 shows data from a batch experiment with 192 pairs of carbon aerogel electrodes (individual cells), a fixed 60 liter volume of ground water, and complete recycle at a rate of 1 liter per minute. The voltage was gradually increased from 0 to 1.2 V. It was found that chromium electrosorption initiates at cell voltages less than or equal to 0.6 V. The concentration of total chromium in the water dropped from an initial level of 25 ppb to 6 ppb at a cell voltage of 0.8 V. The corresponding electrosorption capacity was approximately 5.9×10^{-6} g-Cr g-CAC⁻¹. The concentration then dropped to 4 ppb at 1.0 V and to 3 ppb at 1.2 V. These equilibrium levels corresponded to 6.6×10^{-6} and 6.9×10^{-6} g-Cr g-CAC⁻¹, respectively. The electrosorption capacity given in Table 3, 1.4×10^{-4} g-Cr g-CAC⁻¹ at 1.2 V and 35 ppb, is greater than that determined during this batch experiment. To some extent, this is attributable to the differences in equilibrium chromium concentrations, 35 verses 3 ppb. If a linear isotherm is assumed (Equation 3), the electrosorption capacity at 1.2 V determined during this batch experiment can

be extrapolated to an equilibrium concentration of 35 ppb. The resulting value is 0.81×10^{-4} g-Cr g-CAC^{-1}, which is 58% of the value found in Table 3. Given the cumulative effects of electrolysis in the batch experiment, such as the reduction of dissolved oxygen and Cr(VI), as well as the electrolysis-induced variations in pH, the agreement is considered to be very good. Such effects were less pronounced in the field test since there was no recycle.

Independent measurements of 1,1-dichloroethene (DCE), chloroform (CHCl$_3$), trichlroethene (TCE), and Freon 113 were made by LLNL and an outside laboratory. The feed stream was known to be contaminated with TCE. The measured concentrations of these organic contaminants (with the exception of Freon 113) were well below 30 ppb, with typical measurements of 5 to 10 ppb. A typical measured concentration for Freon 113 was approximately 40 ppb. Some transients in concentration were observed, but the results are inconclusive. There is no indication that the adsorption of these organic species interfered with chromium removal.

Discussion

Cr(VI) Bound to Anode. In regard to Figures 2 and 3, it appears that much of the Cr(VI) [in the form of $HCrO_4^-/CrO_4^{2-}/Cr_2O_7^{2-}$] was electrosorbed on the carbon aerogel anodes during polarization at 0.9 and 1.2 V. Simultaneously, some of the Cr(VI) was reduced to Cr(III) on the cathodes. A fraction of the cathodically-generated Cr(III) was transported back into the flowing stream, while the remainder was electrosorbed on the cathode or held in the cathodic double layer. The parasitic current associated with the reduction of dissolved oxygen, and the current associated with double-layer charging, was orders-of-magnitude greater than the diffusion-limited current associated with Cr(VI) reduction to Cr(III). Thus, rate determinations based upon the measured current could not be made. As shown in Figure 6, none of the Cr(VI) was released during the initial attempt to regenerate by discharging the cells at 0 V. However, a significant amount of Cr(III) was released. Reverse polarization at -1.2 V was required for the release of bound Cr(VI). Several mechanisms have been postulated to explain the absence of Cr(VI) in the outlet stream during the first regeneration step, as well as the pulses of Cr(VI) observed during the second and third regeneration steps (reverse polarization at -1.2 V followed by discharge at 0 V). One of the most plausible involves the cathodic reduction of functional groups on the surface of the carbon aerogel electrodes that served as anodes during chromium removal. The relative irreversibility Cr(VI) adsorption on the carbon aerogel anodes may be due to the formation of a bond between the hydrochromate, chromate and dichromate oxyanions with functional groups on the carbon surface. Cathodic reduction of these functional groups would release bound Cr(VI) anions, allowing them to redissolve into the electrolyte. It is evident that Cr(VI) anions such as hydrochromate, chromate and dichromate are not removed from the ground water by a simple electrostatic (capacitive charging) mechanism. The electrosorption process involves some type of bond formation.

Selectivity of Carbon Aerogel Electrodes. Alkali metal cations such as Na$^+$, K$^+$, Ca^{2+} and M^{2+} are present at ppm levels. The selectivity of the chromium ions over these ions is great, in that ppb levels of Cr are removed in the presence of 530 ppm TDS. No other heavy metals, except for low levels of Zn, were detected during the experiment. In experiments discussed elsewhere,

it has been shown that U, Pb, Cd and other heavy metals, all at very low-concentrations, can be selectively removed from sea water. It has also been shown that Cu, Zn, Cd, and Pb can be selectively removed from 0.1 M KNO_3 solutions [48]. If one assumes a simple adsorption isotherm, $Y = KC$, where Y is the electrosorption capacity at equilibrium (g-M g-CAC^{-1}), C is aqueous concentration at equilibrium (g-M cm^{-3}), and K is the equilibrium constant (cm^3 g^{-1}), the equilibirium constant can be used as an indication of relative selectivity. From the data in Table X below, it appears that the selectivity for Cr removal is comparable to that for Cu removal, and greater than the selectivities for removal of Zn, Cd, and Pb.

Table 3. A comparison of selectivities for heavy metal (M) adsorption on aerogel (CAC).

Metal Impurity	Feed Stream	Initial Concentration	Final Concentration	Electrosorption Capacity - Y	Equilibirium Constant - K
		(ppb)	(ppb)	(g-M g-CAC^{-1})	(cm^3 g-CAC^{-1})
Cd	0.1 M KNO_3	1050	500	2.6×10^{-4}	5.1×10^{2}
Zn	0.1 M KNO_3	1140	240	4.2×10^{-4}	1.7×10^{3}
Pb	0.1 M KNO_3	950	150	3.7×10^{-4}	2.5×10^{3}
Cu	0.1 M KNO_3	980	41	4.3×10^{-4}	1.0×10^{4}
Cr	530 ppm TDS	35	8	1.4×10^{-4}	1.8×10^{4}

Note that the electrosorption capacities given in Table 3 are based on the carbon mass of both CAC electrodes (anode and cathode). The values found in Reference 48 were based upon the carbon mass of the anode (or cathode) alone, and had to be divided by two before inclusion in Table 3. Values of the electrosorption capacity for NH_4ClO_4 on pairs of CAC electrodes are found in Table 1 of Reference 26. At a cell voltage of 1.2 V and and equilibrium (final) concentration of 39 ppm, the electrosorption capacity on 48 pairs of CAC electrodes was found to be approximately 2.0×10^{-5} equivalents of NH_4ClO_4 per gram of carbon, or 2.35×10^{-3} grams per gram of carbon (anode and cathode). Regression analysis of the NH_4ClO_4 data showed that the observed electrosorption capacity was proportional to $C^{0.4337}$, where C is the concentration of NH_4ClO_4. This is close to the $C^{0.5}$ dependence predicted by the Gouy-Chapman Theory for double-layer charging. Though a linear isotherm is not appropriate here, a "selectivity ratio" comparable to the equilibrium constants presented in Table 3 can be calculated. A selectivity ratio (pseudo K value) of 6.0×10^{1} cm^3 g-CAC^{-1} is calculated for NH_4ClO_4 electrosorption on CAC, based upon the observed electrosorption capacity and liquid-phase concentration at equilibrium. By comparing the K values for Cu, Zn, Cd, Pb and Cr to the selectivity ratio calculated for NH_4ClO_4, it is concluded that the selectivities for the heavy metal are substantially greater than the selectivity for this dissolved salt, whose ions are held at the carbon aerogel surface by electrostatic forces alone. Similar conclusions can be reached with data for other dissolved salts, including NaCl, $NaNO_3$, and Na_2SO_4.

Wetability of Carbon Aerogel. Electrolytes, including the well water studied here, appear to adequately wet and penetrate the CAC sheets. Adequate pore size may have promoted good wetability. No measurement of the surface tension has been made, though such measurements would be interesting. Since a precise measurement of contact angle in such a nanoporous

material may not be possible, a more creative approach may be needed. Perhaps the relationship between differential capacitance and surface tension could be exploited. Any differences between the wetability of CAC sheets and other carbon-based materials may be due to the effects of the unique nanostructure of carbon aerogel on the free energy of the surface. Additional insight is needed in this area.

Other Applications and Process Scaleup. There are other similar applications for carbon aerogel electrodes, such as the removal of chromium from rinse water in the electroplating industry. The equipment for a particular application should be sized in a manner similar to that used for ion exchange columns. The time-average mass balance across a stack of CAC elecrodes is:

$$F(C_{Cr-in} - C_{Cr-out})\tau_{Cr-B} = S_{CAC}\,\sigma_{Cr-CAC} \qquad [2]$$

where F is the feed rate of contaminated water to the electrochemical cell, C_{Cr-in} is the concentration of chromium in the feed, C_{Cr-out} is the concentration of chromium in the product, τ_{Cr-B} is the effective breakthrough time (time between regeneration cycles), S_{CAC} is the superficial (sheet) area of the adsorbing CAC electrode, and σ_{Cr-CAC} is the corresponding electrosorption capacity, based on the superficial (sheet) area. It is evident from the data presented in Figure 7 that the 144 g (1.36 m^2 or 14.6 ft^2) of CAC sheet used in this experiment reached equilibrium with the liquid phase (35 ppb) after the adsorption of 20×10^{-3} grams of chromium. This gives an estimated adsorption capacity of 1.29×10^{-4} grams of chromium per gram of CAC sheet (anode and cathode), or 1.50×10^{-6} grams of chromium per square centimeter of CAC sheet (anode and cathode). The electrosorption capacity for chromium on carbon aerogel is concentration dependent. Though there is insufficient data to establish the exact functionality of the isotherm (Langmuir, Frumkin, etc.) near saturation of all available surface sites, a simple linear form can be assumed at low coverage to enable a rough comparison of the selectivities for several impurities (Cr, Cu, Zn, Pb, and Cd):

$$\sigma_{Cr-CAC} = K_{Cr-CAC}\,C_{Cr} \qquad [3]$$

The validity of using a simple linear isotherm, which assumes low coverage, is established by calculating the number of atoms per unit of active surface area. It is well known that most surfaces become saturated with adsorbates in the range of 10^{13} to 10^{15} atoms cm^{-2}, depending upon the structure of the surface, the size of the adsorbate, and the environment [49-53]. A typical coverage is approximately 10^{14} atoms cm^{-2}. Based on the measured electrosorption capacity of 1.39×10^{-4} g-Cr g-CAC^{-1}, the number of adsorbed Cr atoms per gram of carbon aerogel is calculated to be approximately 1.61×10^{18}. The range of BET surface area available with CAC sheets is approximately 400 to 1100 m^2 g^{-1}, though values as high as 2600 m^2 g^{-1} have been achieved through thermal activation. If one assumes that the BET surface area is an order-of-magnitude estimate of active surface area, a surface coverage of 4.0×10^{11} atoms cm^{-2} is calculated with 400 m^2 g^{-1}, while 1.5×10^{11} atoms cm^{-2} is calculated with 1100 m^2 g^{-1}. Since it is possible that only a fraction of the BET surface area is accessible to the electrolyte and dissolved chromium, it is futher assumed that the active surface area is only 10 percent of the BET surface area. In this case, the maximum coverage would be expected to be about 4.0×10^{12} atoms cm^{-2},

which translates into a surface coverage of about 4 percent ($\theta = 0.4$). Therefore, the assumption of a linear isotherm appears to be reasonable. Detailed studies of the adsorption of heavy metals on carbon-based materials with high surface area, such as carbon aerogel, are recommended as a fruitful area for future study. Adsorption isotherms applicable over a the entire range of surface coverage should be established. Detailed engineering studies of electrosorption processes based upon carbon aerogel electrodes are presented elsewhere [54].

Secondary Waste from Ion Exchange. The ground water beneath the LLNL site has unacceptable levels of TCE and Cr(VI). Two large ion exchange columns are now used to remove 35 ppb Cr(VI) from very hard ground water (530 ppm TDS) at LLNL Treatment Facility C. These columns contain 1.7 m^3 (60 ft^3) of mixed ion exchange resin and have a design capacity of 227 liter min^{-1} (60 gpm). Regeneration with 2,271 liters (600 gallons) of concentrated salt solution having 170,000 ppm TDS is required every 30 to 45 days. Assuming an average time between regeneration cycles of 37.5 days, the average rate of liquid waste generation is 61 liter day^{-1} (16 gpd) which results in a solid waste generation rate of 10.3 kg day^{-1} (22.7 lb day^{-1}). Solid waste from the ion exchange process is from two sources, dissolved inorganic salts in the spent chemical regenerant (170,000 ppm TDS), and the spent ion exchange resin. Ultimately, such liquids are evaporated to dryness and shipped to landfill sites for disposal.

Secondary Waste from Electrosorption Process. It has been demonstrated that reversible electrosorption of chromium ions on carbon aerogel electrodes can be used as a means of continuously removing Cr(VI) contamination from this stream. This reversible aerogel-based electrosorption process eliminates the secondary wastes associated with the chemical regeneration of ion exchange columns. Unlike ion exchange, no acids, bases, or salt solutions are required for regeneration of the system. Regeneration is accomplished by electrically discharging the cell. This initial testing was done with a relatively small stack of electrodes with only 1.36 m^2 (14.6 ft^2) of CAC sheet. The concentration of Cr(VI) in the outlet stream was maintained below the acceptable level of 11 ppb for approximately 50 hrs, at which time a gradual breakthrough was experienced. A total of 300 liters (79 gallons) of Cr(VI)-contaminated water was treated before regeneration was required. The rate of liquid and solid waste generation for a carbon aerogel system can be estimated from the results of the initial field test. Given that 1.36 m^2 (14.6 ft^2) of CAC sheet is sufficient to process Cr(VI)-contaminated well water at a flow rate of 0.1 liter min^{-1}, the quantity needed to process the entire TFC feed of 57 liter min^{-1} (15 gpm) is approximately 770 m^2 (8,290 ft^2). Regeneration by reverse polarization and electrical discharge would be required every 50 h (2.08 days). If one assumes zero flow during regeneration, which is possible but not demonstrated during this study, the average rate of liquid waste generation should be approximately 273 liter day^{-1} (72 gpd) at 530 ppm TDS, which is due to the liquid inventory trapped inside of the electrochemical cells during discharge. This is based upon the liquid inventory in the electrochemical cell used for this study, which was approximately 1 liter (1,063 ml). All adsorbed chromium is released into this liquid volume. Approximately 144 g day^{-1} (0.32 lb day^{-1}) of solid inorganic residue would then be produced by evaporating the liquid waste to dryness. This solid waste would have to be sent to a landfill for burial. Ultimately, cells should be redesigned to minimize the quantity of retained liquid. For example, a 10X reduction in electrode separation would lower the rates of liquid and solid waste

generation to less than 27 liter day^{-1} (7 gpd) and 14 g day^{-1} (0.03 lb day^{-1}), respectively. Note that zero flow was not used in the field test since that would have precluded the sampling necessary to observe and elucidate the regeneration process. The flow rate was selected to provide the sample volume necessary for analysis (the entire flow from the cell was diverted into sample containers to obtain sufficiently large samples for the battery of analyses being performed at the time). In other laboratory experiments, regeneration has been done with trapped volumes of water. The effect of flow on regeneration should be investigated in the future. To minimize liquid waste, one would strive to keep the flow as small as possible.

Advantages of Carbon Aerogel Electrodes. Carbon aerogel was invented by LLNL and has a unique combination of properties that make it an outstanding electrode material for separation processes based upon reversible electrosorption. These attributes include a monolithic structure with relatively large pores, exceptionally low electrical resistivity (40 mΩ-cm), and high BET surface area (400 to 2600 m^2 g^{-1}). The resistance of a typical carbon aerogel electrode is much less than a comparable electrode made of activated carbon. For example, the "through resistance" of activated carbon electrodes with polymeric binders is in the range of 1 to 3 Ω [10], compared to ~10 $\mu\Omega$ for an aerogel electrode. The value for the aerogel electrode is based on a measured resistivity of 40 mΩ cm [34]. Attempts to make direct measurements of the "through resistance" with a standard digital ohm meter were not possible since the electrode conductivity was so high that it appeared as if the leads were shorted together. Such high conductivity could eliminate the need for expensive metallic substrates. It should be noted that the elimination of substrates would also be beneficial in processes designed for radioactive solutions since decontamination would be simplified. The monolithic structure prevents entrainment in flow and enables fabrication of very thin electrodes ($\leq$ 0.0127 cm). Large pores are necessary for wetting and formation of the electric double layer. In the application of monolithic carbon aerogel electrodes to capacitive deionization (CDI), benefits include enhanced electrosorption capacity due to the immense specific surface area and complete immobilization of the porous carbon matrix. Carbon aerogel electrodes can be fabricated that have more accessible surface area than comparable activated carbon powders, thereby enabling greater electrosorption. The exceptional electrical conductivity and thin construction of carbon aerogel electrodes minimize potential drop. Therefore, more ions can be electrosorbed on a unit of carbon aerogel surface area than on a comparable unit of activated carbon surface area. In deep packed beds of carbon, the potential can drop to levels where the electrosorption process is not very effective. Unlike beds of activated carbon powder, monolithic sheets of carbon aerogel are not entrained in the flowing fluid stream. Consequently, the need for porous separators are eliminated. The electrolyte flows in a channel between adjacent anodes and cathodes and does not experience the high pressure drop associated with flow through packed beds. Since there is no need for polymeric binders, the monolithic carbon aerogel electrodes are relatively resistant to both chemical attack and radiation-induced degradation, provided that polymer-based cements are not used. The economic viability of this aerogel-based separation process depends upon the life of the carbon aerogel electrodes. To gain insight into electrode life, studies with new, aged, and rejuvenated electrodes are presented. Note that the outlet stream purity that can be achieved with this process is limited by the number of electrode pairs. In a separation process, the highest purity is achieved with infinite theoretical stages.

Mass Production of Aerogel. The capital costs of this process have been dominated thus far by the cost of carbon aerogel. Approximately 372 m^2 (4000 ft^2) of carbon aerogel sheet has been mass produced for construction of a relatively large system. Such a system should be sufficient to treat a large fraction of the water now flowing through the TFC, approximately 82,192 kilograms of well water between regeneration cycles. In regard to the cost of the carbon aerogel (CAC sheets), the first material synthesized in a laboratory at LLNL and was extremely labor intensive. The cost to produce 6.86 cm x 6.86 cm squares was roughly $6 per cm^2 ($5,600 per ft^2). Eventually, the synthesis process was successfully transfered to a small, commercial producton facility. This facility made relatively large batches of the material at an apparant cost of $0.05 per cm^2 ($50 per ft^2). One can estimate much lower costs with the following assumptions: a less expensive, high-volume source of carbon paper; large volume acquisition of resorcinol and formaldehyde (or a less expensive alternative); and recycle of the acetone solvent.

Summary

Reversible electrosorption on carbon aerogel electrodes has been used as a means of selectively removing various chromium species from ground water. The first successful demonstration at LLNL Treatment Facility C has been completed. Three small stacks of carbon aerogel electrodes (48 double-sided electrodes eached) polarized at +1.2 V were used to continuously remove trivalent and hexavalent chromium from raw, untreated ground water. After saturation of the stack, regeneration was accomplished by the following sequence: (a) cell discharge at 0 V; (b) reverse polarization at -1.2 V; and (c) cell discharge at 0V. The cells were undivided (no membranes were used). The total quantity of carbon aerogel sheet used in the experiment was about 144 grams (1.36 m^2 or 14.6 ft^2). Chromium levels in the effluent were maintained at acceptable levels for more than 50 h (300 liters of treated water). If regeneration with zero flow can be demonstrated, it should be possible to reduce the rate of solid waste generation can from the 10.3 kg day^{-1} now required for ion exchange (25% of design capacity) to approximately 0.144 kg day^{-1} with the carbon aerogel process. We now have an inventory of over 372 m^2 (4000 ft^2) of carbon aerogel sheet, which should be sufficient to treat 82,192 liters (21,713 gallons) of well water between regeneration cycles. This is expected to be enough to treat 48% of the water now flowing through Treatment Facility C.

Future Work

Several additional experiments are envisioned to optimize the treatment process for scale-up, to better define the nature of the chromium reduction and removal reactions, and possibly to improve the performance of electrosorption as a general approach for the remediation of trace metals in ground and waste waters. These experiments are as follows: (1) further on-line tests of the effects of polarization voltage during the treatment and regeneration cycles; (2) tests of water flow rate during the treatment cycle, to determine the maximum flow rate at which remediation is effective; (3) surface analysis of the electrodes after a treatment cycle to determine the location and possibly the speciation of the chromium that is removed from the waste stream; and (4) tests using a stack of cells constructed with narrower gaps between the electrodes, to decrease the volume of solution within the cells.

More data are needed to precisely determine the effects of cell voltage on chromium retention during single-pass operation (no recycle). Such an experiment should be performed at a constant flow rate of 100 ml min^{-1} with sequential 4 h periods of operation at 1.0, 1.3, and 1.5 V. Note that sufficient data at 0.9 and 1.2 V have already been obtained. A study of the effects of flow rate should also be conducted. This experiment should be conducted at a constant cell voltage of 1.2 V with sequential 3 h periods of operation at 200, 500, 1000, and 1500 ml min^{-1}. A regeneration sequence similar to the one used in this study should be used, but with minimal waiting periods.

Preparation of the electrodes for surface analysis, to learn more about the fate of the chromium, expeirments should be done in the laboratory with a smaller stack of electrodes and synthetic water, although actual well water would be more relevant. After testing, the electrodes should be removed from the cell and prepared for surface analysis. X-ray fluorescence (XRF) and Auger electron spectroscopy (AES) analysis should be done to measure the total chromium on each anode and cathode. Such measurements should be made on electrodes removed immediately after the treatment cycle, as well as on electrodes removed immediately after the regeneration cycle.

Experiments with cells divided by either anion or cation-exchange membranes should be done. In addition to electrosorption, electrolytic reduction should be investigated as a means of achieving acceptable Cr(VI) levels. The use of such a cell, and electrolytic reduction of the Cr(VI) to Cr(III), could obviate, or at least extend the time before the need for regeneration. Electrosorption with a divided cell may shed more light on the mechanism of the chromium removal.

Acknowledgements

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Figure Captions

Figure 1. Schematic representation of an electrochemical cell similar to that used for experiments, except with 12 double-sided electrodes.

Figure 2. Concentrations of total Cr and Cr(VI) during first 28 h of LLNL TFC experiment. The flow rate was 100 ml min^{-1}.

Figure 3. Concentrations of total Cr and Cr(VI) during first 250 h of LLNL TFC experiment. The flow rate was 100 ml min^{-1}.

Figure 4. Measurements of conductivity and cell voltage during first 50 h of LLNL TFC experiment. The flow rate was 100 ml min^{-1}.

Figure 5. Measurements of pH and cell voltage during first 50 h of LLNL TFC experiment. The flow rate was 100 ml min^{-1}.

Figure 6. Regeneration of carbon aerogel electrodes by electrical discharge and reverse polarization. Initially, the flow rate was 100 ml min^{-1}, but was increased to 1000 ml min^{-1} during the reverse polarization at -1.2 V.

Figure 7. Total Cr retained by carbon aerogel electrodes during experiment at LLNL TFC. Initially, the flow rate was 100 ml min^{-1}, but was increased to 1000 ml min^{-1} during the reverse polarization at -1.2 V.

Figure 8. The effect of cell voltage on Cr removal during batch experiment with 60 liters of contaminated well water. The water was continuously recycled at a rate of 1000 ml min^{-1}.

Positive Terminal

Gasket Material

Header

Contaminated Water

Negative Terminal

Carbon Aerogel Composite Sheet

Product Water

Titanium Support

Cell Voltage (V)

Cell Voltage

Flow = 100 ml min^{-1}

Cr(VI)+Cr(III)

Cr(VI)

Time (h)

Concentration (ppb)

Cell Voltage (V)

Inlet pH

Sample pH

Outlet pH

Flow = 100 ml min^{-1}

Cell Voltage

Time (h)

pH

Legend:
- Cr(III+VI)
- Cr(VI)
- Cr(III)

Discharge at 0.0 V & 100 ml min^{-1}

Reverse polarization at 1.2 V & 1000 ml min^{-1}

Discharge at 0.0 V & 1000 ml min^{-1}

Time (h)

Concentration (ppb)

Chromium removal during polarization at
+1.2 V & 100 ml min^{-1}

Chromium release at
0.0 V & 100 ml min^{-1}

Chromium release at
-1.2V & 1000 ml min^{-1}

Chromium release at
0.0 V & 1000 ml min^{-1}

Total Chromium Retained (mg)

Time (h)

Cell Voltage (V)

Concentration (ppb)

Time (h)

Removal

Regeneration

Cell Voltage

6 ppb equilibrium at 0.8 volts

4 ppb at 1.0 volts

3 ppb at 1.2 volts

Cr(III+VI)

Cr(VI)